Chapter 6: Neutralizing the Threat of Acid Rain

Is normal rain acidic?

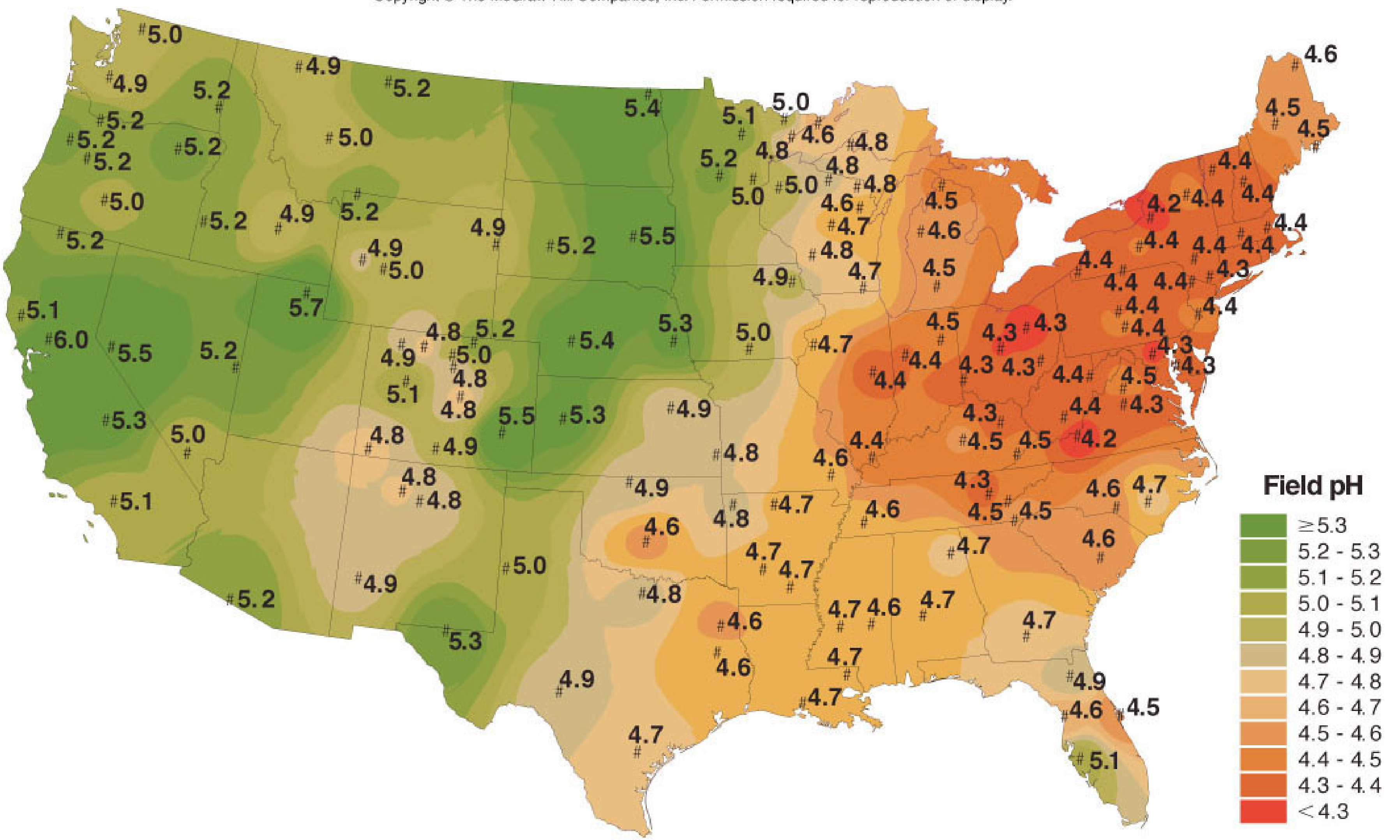
Is acid rain worse in some parts of the country?

Is there a way to "neutralize" acid rain?

Acid Rain

- The problem
  - Regional atmospheric problem
  - Lakes, forests, and structures affected
- Mechanism
  - Acid-base chemistry
- Solution
  - 1852 first noted
  - 1980 Data collection: NAPAP
  - 1990 Clean Air Act

Field pH

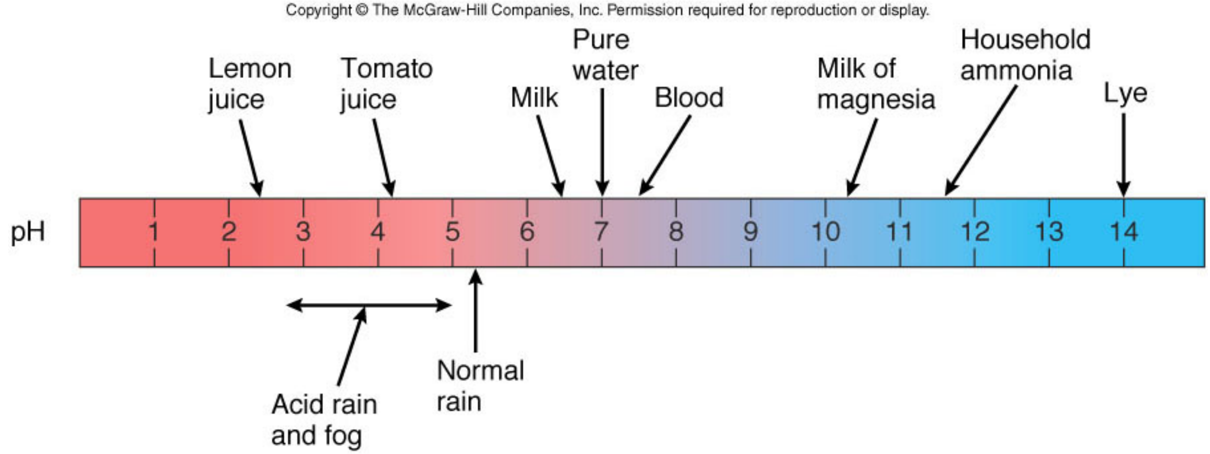


(Source: National Atmospheric Deposition Program National Trends Network. Taken from http://nadp.sws.uiuc.edu)

What does the word *acid* mean to you?

Visual range 20 miles

Visual range 100 miles



pH of rain

- neutral pH = 7
- Unpolluted rainwater?
- pH = 5.6
- Acid rain pH ~ 4.1
- 1982: fog pH = 1.8!!!
- Tropospheric CO_2 (355 ppm), NO (0.01 ppm), SO_2 (0.01 ppm)

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

Carbonic acid

- Power plants (SO_2) and automobile emission (NO)

$$SO_{2(g)} \xrightarrow{O_2} SO_{3(g)} \xrightarrow{H_2O} H_2SO_4$$ Sulfuric acid

- Marble and limestone

$$CaCO_{3(s)} + H_2SO_4(aq) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + H_2O + CO_2$$

Definition of Acids

One way to define an **acid** is as a substance that releases hydrogen ions, H^+, in aqueous solution.

Since the hydrogen ion has no electron, and only one proton (hence the positive charge), the hydrogen ion sometimes is referred to as a **proton**.

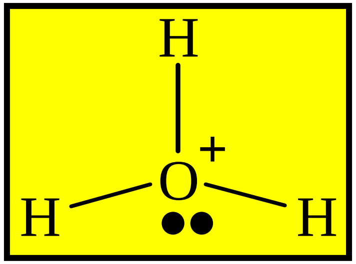
Consider hydrogen chloride gas, dissolved in water:

$$HCl(g) \xrightarrow{H_2O} \underset{\text{(a proton)}}{H^+(aq)} + Cl^-(aq)$$

H^+ ions are much too reactive to exist alone, so they attach to something else, such as to water molecules.

When dissolved in water, each HCl donates a proton (H^+) to an H_2O molecule, forming H_3O^+, the hydronium ion.

The Cl^- (chloride) ion remains unchanged.



Hydronium ion. Often we simply write H^+, but understand it to mean H_3O^+ when in aq. solutions

The overall reaction is:

$$HCl(g) + H_2O(l) \longrightarrow \underbrace{H_3O^+(aq)}_{\text{hydronium ion}} + Cl^-(aq)$$

Strong Acids

- Hydrochloric acid, HCl
- Hydrobromic acid, HBr
- Hydroiodic acid, HI
- Nitric acid, HNO_3
- Sulfuric acid, H_2SO_4
- Perchloric acid, $HClO_4$

Carbonic Acid, a weak acid, is not stable in water:

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

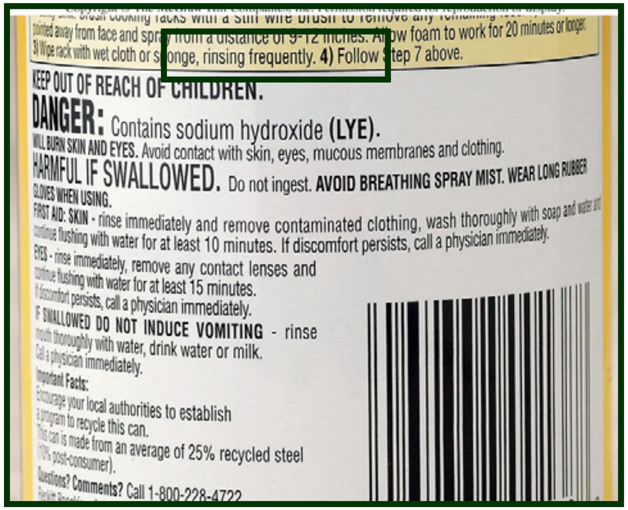
Definition of Bases

The flip side of the story is the chemical opposite of acids: bases.

A **base** is any compound that produces hydroxide ions (OH^-) in aqueous solution.

Characteristic properties of bases:

- Bitter taste (not recommended)
- Slippery feel when dissolved in water
- Turn red litmus paper blue



$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

Sodium hydroxide — Sodium ion — Hydroxide ion

Calcium hydroxide produces 2 equivalents of OH^- :

$$Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$$

What about ammonia (NH_3)? It is a base, but has no OH group.

$$NH_3(aq) + H_2O(l) \longrightarrow NH_4OH(aq)$$ ammonium hydroxide

$$NH_4OH(aq) \xrightarrow{H_2O} NH_4^+(aq) + OH^-(aq)$$

Strong Bases

- Hydroxides of the 1st and 2nd groups of periodic table
  - Potassium hydroxide, KOH
  - Sodium hydroxide, $NaOH$
  - Calcium hydroxide, $Ca(OH)_2$
  - Strontium hydroxide, $Sr(OH)_2$

When acids and bases react with each other, we call this a **neutralization reaction**.

$$HCl(\mathit{aq}) + NaOH(\mathit{aq}) \longrightarrow NaCl(\mathit{aq}) + H_2O(\mathit{l})$$

In **neutralization** reactions, hydrogen ions from an acid combine with the hydroxide ions from a base to form molecules of water.

The other product is a salt (an ionic compound).

Consider the reaction of hydrobromic acid with barium hydroxide.

This reaction may be represented with a molecular, ionic, or net ionic equation:

Molecular:

$$2\ HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\ H_2O(l)$$

Ionic:

$$2\ H^+(aq) + 2\ Br^-(aq) + Ba^{2+}(aq) + 2\ OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2\ Br^-(aq) + 2\ H_2O(l)$$

Net Ionic:

$$2\ H^+(aq) + 2\ OH^-(aq) \longrightarrow 2\ H_2O(l)$$

or by dividing both sides of the equation by 2 to simplify it:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

$$\boxed{2\ HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\ H_2O(l)}$$

How did we go from Ionic to Net Ionic?

Ionic:

$$2\ H^+(aq) + \boxed{2\ Br^-(aq)} + \boxed{Ba^{2+}(aq)} + 2\ OH^-(aq) \longrightarrow \boxed{Ba^{2+}(aq)} + \boxed{2\ Br^-(aq)} + 2H_2O(l)$$

Remove the species that appear unchanged on both sides of the reaction

- these are called **spectator ions.**

$$\boxed{2\ HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\ H_2O(l)}$$

How did we go from Ionic to Net Ionic:

Ionic:

$$2\ H^+(aq) + \boxed{2\ Br^-(aq)} + \boxed{Ba^{2+}(aq)} + 2\ OH^-(aq) \longrightarrow \boxed{Ba^{2+}(aq)} + \boxed{2\ Br^-(aq)} + 2\ H_2O(l)$$

spectator ions

Net Ionic:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

The **pH** of a solution is a measure of the concentration of the H^+ ions present in that solution.

The mathematical expression for pH is a log-based scale and is represented as:

$$\boxed{pH = -\log[H^+]}$$

So for a solution with a

$[H^+] = 1.0 \times 10^{-3}$ M, the pH = $-\log(1.0 \times 10^{-3})$, or $-(-3.0) = 3.0$

Since pH is a log scale based on 10, a pH change of 1 unit represents a power of 10 change in $[H^+]$.

That is, a solution with a pH of 2 has a $[H^+]$ ten times that of a solution with a pH of 3.

$$\boxed{[H^+] = 10^{-pH}}$$

To measure the pH in basic solutions, we make use of the expression

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \quad (\text{at } 25\ {}^oC)$$

where Kw is the ion-product constant for water. Knowing the hydroxide ion concentration, we can calculate the $[H^+]$, and use the pH expression to solve for pH.

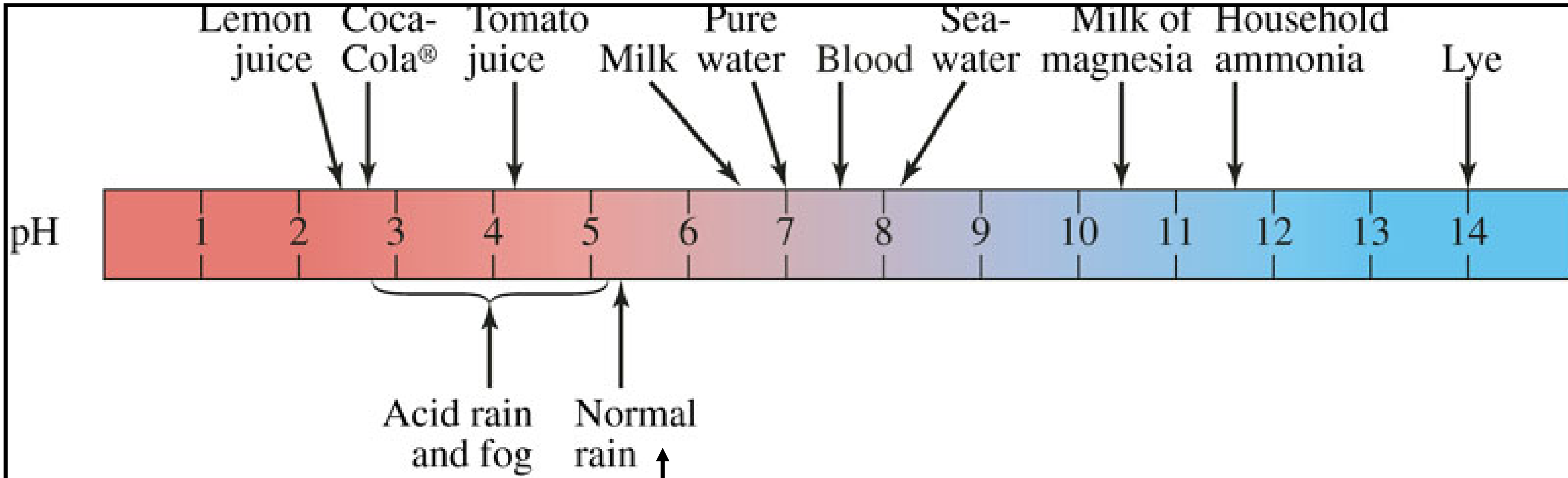
The three possible aqueous solution situations are:

$[H^+] = [OH^-]$ a neutral solution ($pH = 7$)
$[H^+] > [OH^-]$ an acidic solution ($pH < 7$)
$[H^+] < [OH^-]$ a basic solution ($pH > 7$)

pH problems

- In aqueous solution:
  - $[H^+][OH^-] = 1 \times 10^{-14}$
  - pH + pOH = 14 = pKw
  - Group exercises:
    - A: In unpolluted rainwater, what is $[OH^-]$?
    - A: pH = 5.6
    - pOH = 8.4
    - $[OH^-] = -\log(pOH) = 4 \times 10^{-9}$
    - B: How many times more acidic, $[H^+]$, is acid rain than unpolluted rain?
    - B: pH = 5.6 vs. pH = 4.1
    - $= 10^{(5.6/4.1)}$
    - $\approx 10^{1.5}$
    - ≈ 32 times

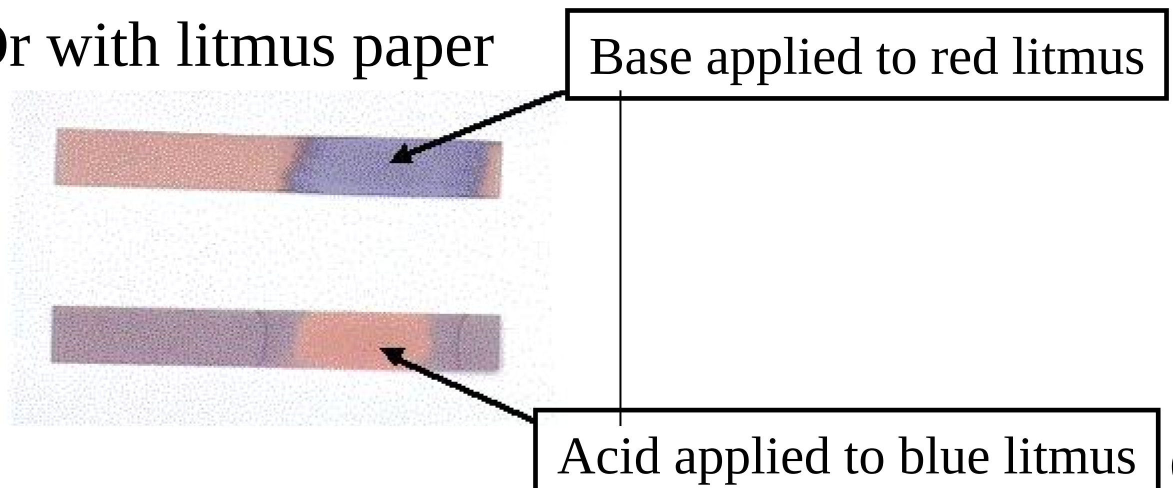
Common Substances and their pH values



Note that "normal" rain is slightly acidic.

Measuring pH with a pH meter

Or with litmus paper



Acid Rain

Why is rain naturally acidic?

Carbon dioxide in the atmosphere dissolves to a slight extent in water and reacts with it to produce a slightly acidic solution of carbonic acid:

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3\,(aq) \quad \text{carbonic acid}$$

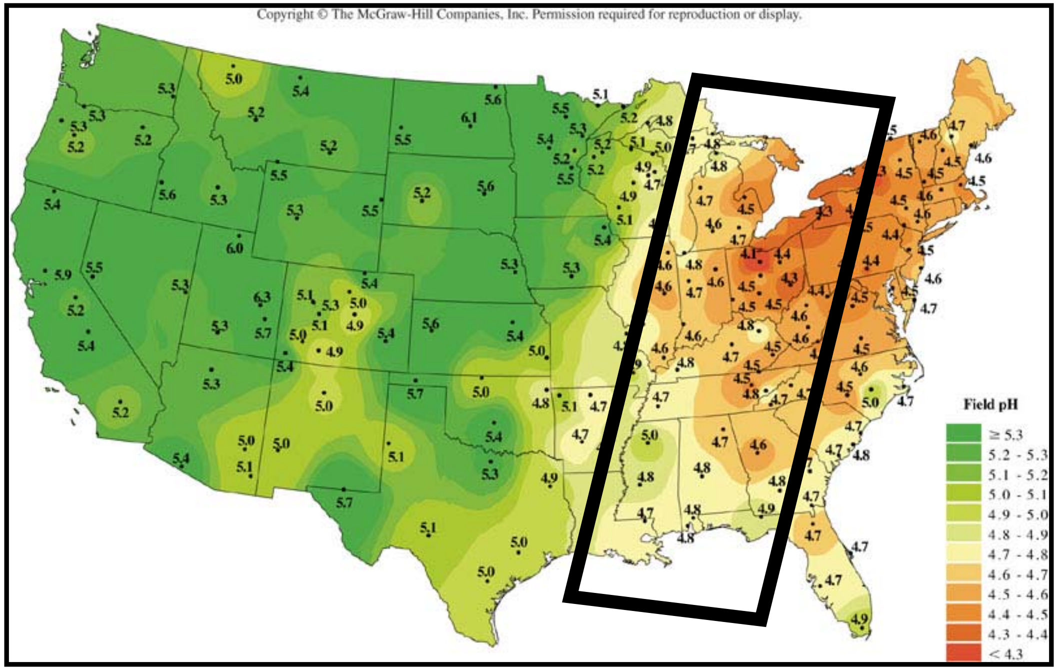
$$H_2CO_3\,(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$$

The carbonic acid dissociates slightly leading to rain with a pH around 5.3

But acid rain can have pH levels lower than 4.3-where is the extra acidity coming from?

The most acidic rain falls in the eastern third of the United States, with the region of lowest pH being roughly the states along the Ohio River valley.

The extra acidity must be originating somewhere in this heavily industrialized part of the country.



Analysis of rain for specific compounds confirms that the chief culprits are the oxides of sulfur and nitrogen:

sulfur dioxide (SO_2), sulfur trioxide (SO_3), nitrogen monoxide (NO), and nitrogen dioxide (NO_2).

These compounds are collectively designated SO_x and NO_x and often referred to as “sox and nox”.

Sulfur dioxide emissions are highest in regions with many coal-fired electric power plants, steel mills, and other heavy industries that rely on coal.

Allegheny County, in western Pennsylvania, is just such an area, and in 1990 it led the United States in atmospheric SO_2 concentration.

The highest **NO*x*** emissions are generally found in states with large urban areas, high population density, and heavy automobile traffic.

Therefore, it is not surprising that the highest levels of atmospheric NO_2 are measured over Los Angeles County, the car capital of the country.

How does the sulfur get into the atmosphere?

The burning of coal.

Coal contains 1-3% sulfur and coal burning power plants usually burn about 1 million metric tons of coal a year!

Burning of sulfur with oxygen produces sulfur dioxide gas, which is poisonous.

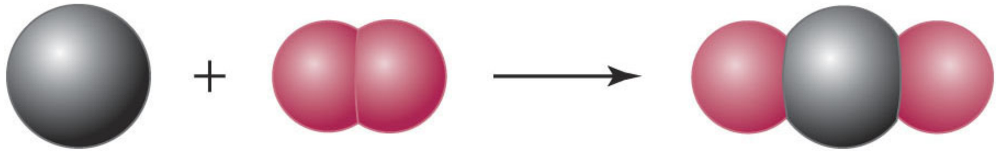
$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

Once in the air, the SO_2 can react with oxygen molecules to form sulfur trioxide, which acts in the formation of aerosols.

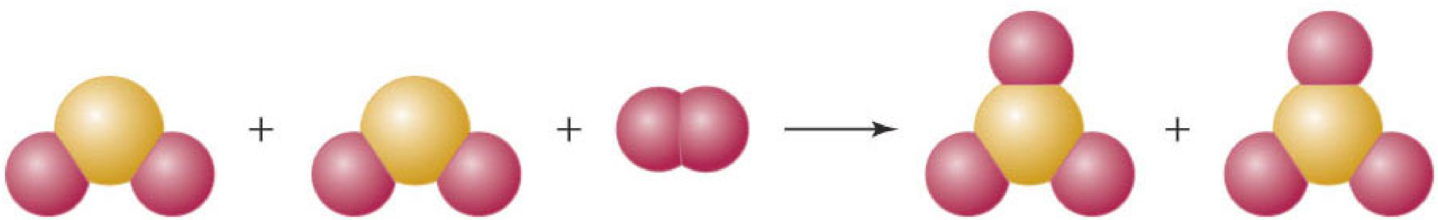
$$2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$$

SO_x reactions

$$S \text{ (in coal)} + O_2(g) \longrightarrow SO_2(g)$$



$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$



$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$ sulfurous acid

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$ sulfuric acid

And then: $$H_2SO_4(aq) \longrightarrow 2\,H^+(aq) + SO_4^{2-}(aq)$$

What about the NOx?

$$4\ NO_2(g) + 2\ H_2O(l) + O_2(g) \longrightarrow 4\ HNO_3(aq)$$

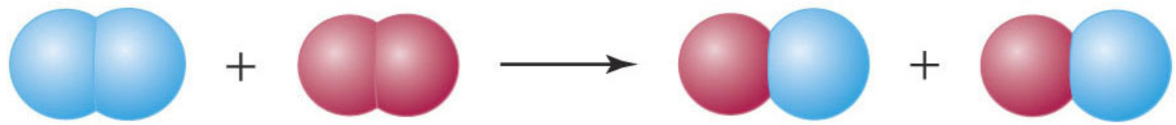
nitric acid

Like sulfuric acid, nitric acid also dissociates to release the H^+ ion:

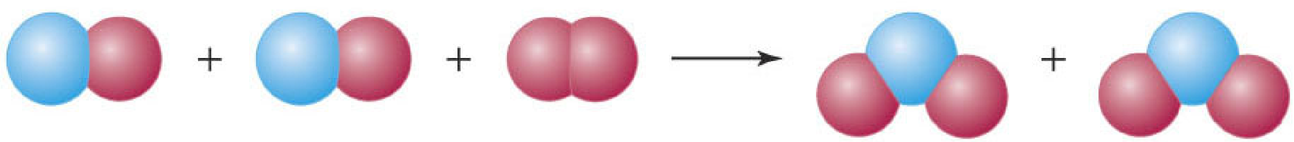
$$HNO_3\ (aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

NO_x Reactions

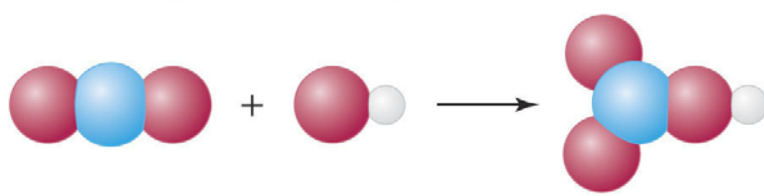
$$\text{Energy} + N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$$



$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$



$$NO_2(g) + OH(g) \longrightarrow HNO_3(l)$$



How much SO_2 and NOx are we emitting in this world?

Table 6.1 Estimated Global Emissions of Sulfur and Nitrogen Oxides

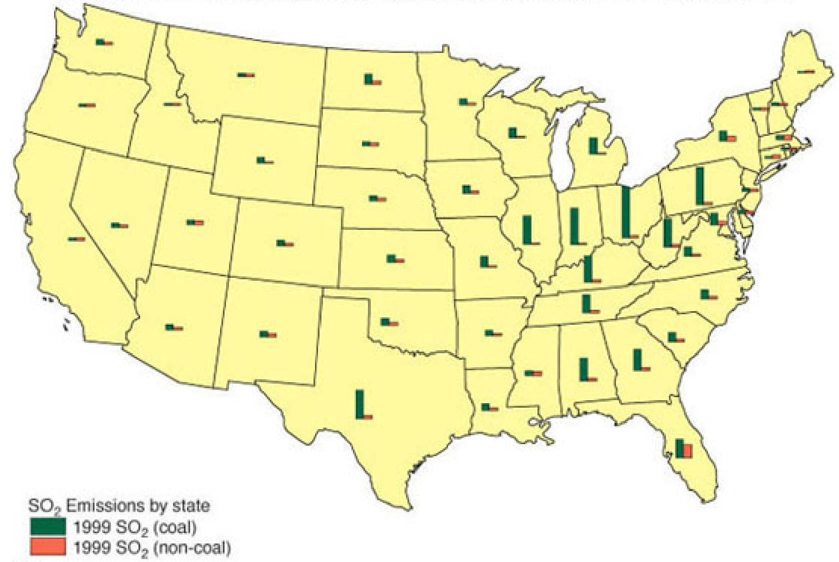
	SO_2*	NO_x†
Natural Sources		
Oceans‡	25	
Soil		5.6
Volcanoes	10	
Lightning		5.0
Subtotal	35	10.6
Anthropogenic Sources		
All sources	69	
Fossil fuel combustion		33
Biomass combustion		7.1
Aircraft		0.7
Subtotal	69	40.8
Total	104	51.4

Source: *Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, 2001, p. 315 and p. 260. Reprinted with permission.

* In units of 10^{12} g sulfur/year.

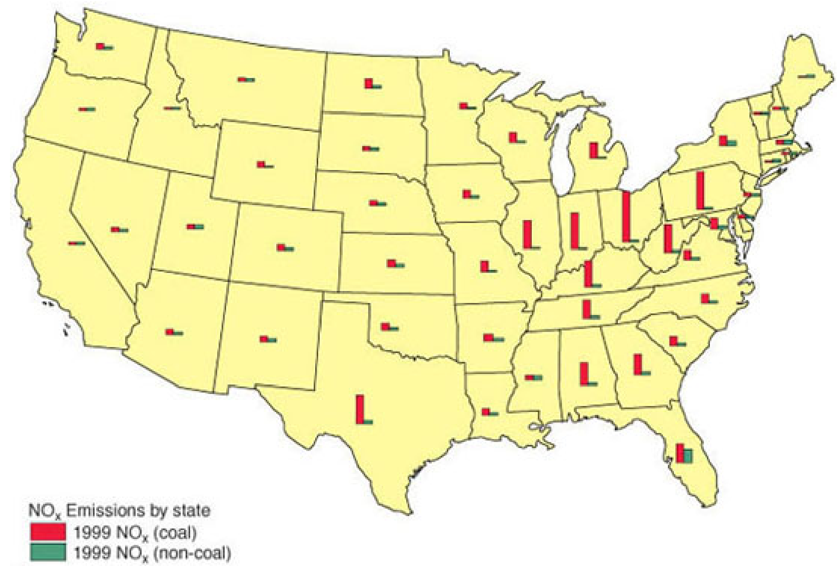
† In units of 10^{12} g nitrogen/year.

‡ Sulfur is emitted from oceans in the form of dimethyl sulfide rather than SO_2.



(a)

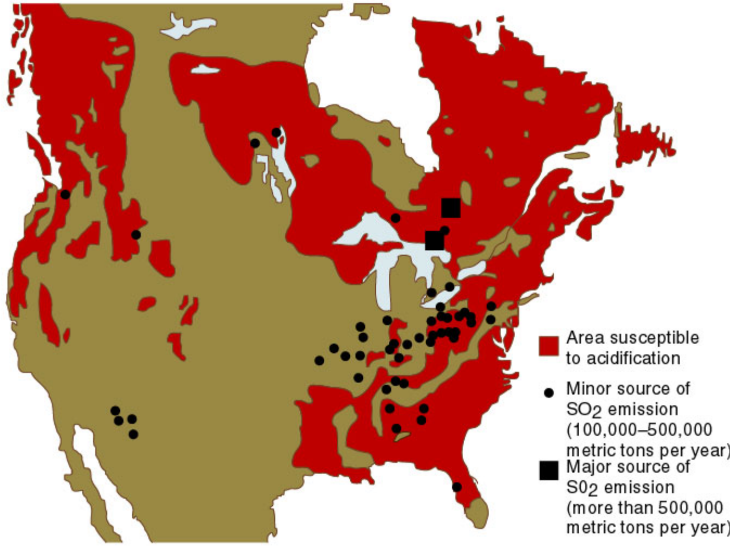
Source: http://www.epa.gov/airmarkets/emissions/score99/figureb1.html.



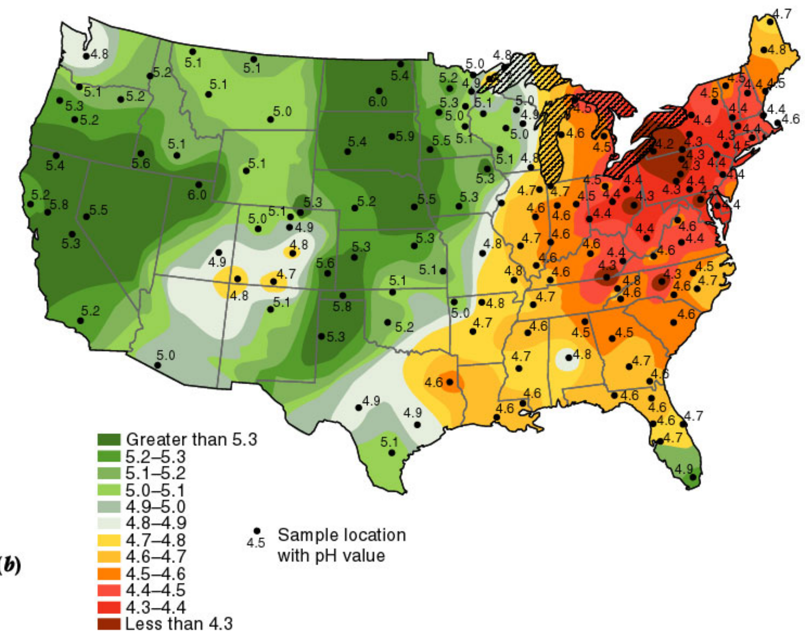
(b)

Source: http://www.epa.gov/airmarkets/emissions/score99/figureb2.html.

Areas in Canada and the United States that are sensitive to acid rain.



(*a*)



(*b*)

n Wiley and Sons Publishers

Effects of acid rain: damage to marble

1944 At present

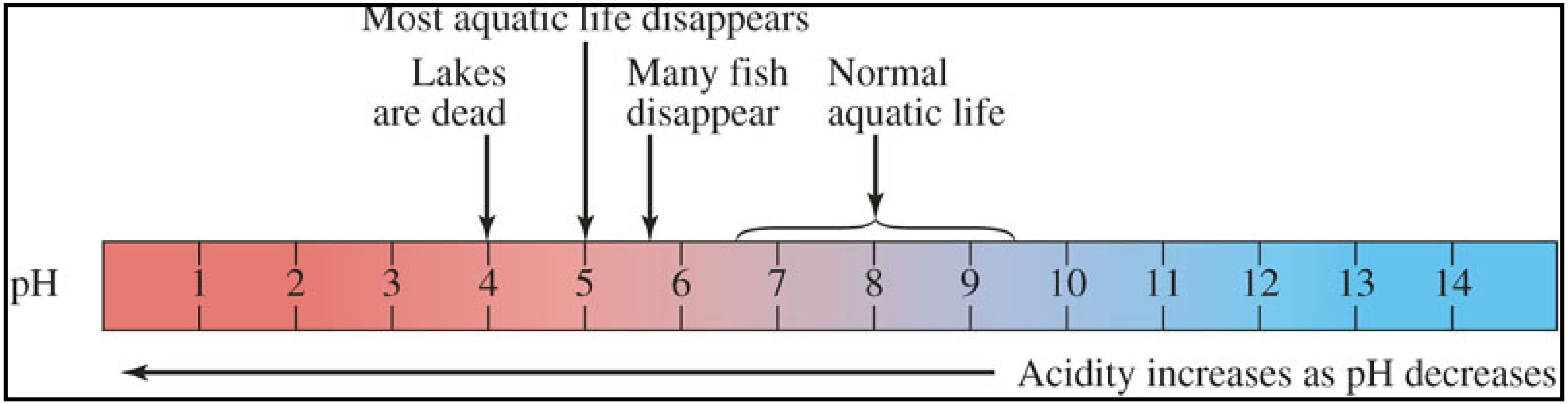
These statues are made of marble, a form of limestone composed mainly of calcium carbonate, $CaCO_3$.

Limestone and marble slowly dissolve in the presence of H^+ ions:

$$CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

Effects of acid rain: damage to forest

Effects of acid rain: damage to lakes and streams



“They stop at Overlooks, idling their engines as they read signs describing Shenandoah’s ruggedly scenic terrain:

Hogback, Little Devil Stairs, Old Rag, Hawksbill.

Jammed along the narrow road, the cars and motor homes add to the miasmic summer haze that cloaks the hills.”

Ned Burks,

Environmental writer
describing Skyline Drive in Virginia

Visual range 20 miles   Visual range 100 miles